



Short communication

Electrochemical lithium ion intercalation into graphite electrode in propylene carbonate-based electrolytes with dimethyl carbonate and calcium salt



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H I G H L I G H T S

- Electrochemical properties of graphite electrodes in PC/DMC electrolyte were studied.
- Exfoliation of graphite took place when the amount of DMC was small.
- Li^+ ion intercalation/de-intercalation took place when the amount of DMC was enough.
- Li^+ ion intercalation is achieved in lower viscosity electrolyte than previous study.

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Electrochemical intercalation of Li^+ ions into graphite electrodes in propylene carbonate (PC)-dimethyl carbonate (DMC)-based electrolytes containing Ca^{2+} ions was studied. The molar ratio of PC, Li^+ ion, and Ca^{2+} ion was $\text{PC}:\text{Li}^+:\text{Ca}^{2+} = 12:1.0:0.5$. Intercalation of Li^+ ions became possible by adding DMC to the PC-based electrolytes containing Ca^{2+} ions: Li^+ ion intercalation did not take place when the amount of DMC was $\text{DMC}/\text{PC} = 6$ (molar ratio) and below, and Li^+ ions intercalated when the amount of DMC was above $\text{DMC}/\text{PC} = 8$. Intercalation of Li^+ ions did not take place in PC-DMC-based electrolyte of no Ca^{2+} ions, and both Ca^{2+} ion and DMC were necessary for Li^+ ion intercalation. Successful Li^+ ion intercalation can be attributed to smaller solvation number of PC on Li^+ ions by addition of DMC and Ca^{2+} ions to the PC-based electrolyte.

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1. Introduction

A world wide concern on exhaustion of fossil fuels raises an interest on R & D for electric vehicles (EVs). Lithium-ion batteries (LIBs) have attracted attention as a power source of EVs because of its high energy density and high working voltage. Ethylene carbonate (EC) is employed as a main electrolyte of LIB because of its ability to form solid electrolyte interphase (SEI) [1,2], which is essential for stable Li^+ ion intercalation into a graphite electrode. However, high melting point of EC at 36°C [3] results in poor ionic conductivity at low temperature, and it can be a problem for the usage of electric vehicles in a cold area.

One of the ways to improve ionic conductivity at low temperature is to replace EC with an organic solvent with low melting

point. The melting point of propylene carbonate (PC) is -49°C [3], and PC-based electrolytes should maintain better ionic conductivity than EC-based electrolytes in a cold area. The problem of using PC as a main electrolyte of LIB is that exfoliation of graphite takes place. The possible reasons for the failure of Li^+ ion intercalation in PC-based electrolytes are steric hindrance of PC-solvated Li^+ ions [4,5] and gas evolution by reduction of PC [6,7], but the mechanism for graphite exfoliation is still under dispute.

Continuous exfoliation of graphite in PC-based electrolytes prevents Li^+ ion intercalation into graphite. Thus, a common way to enable Li^+ ion intercalation is to form 'good' SEI with film forming additives before graphite exfoliation takes place. Organic components such as chloroethylene carbonate [8], ethylene sulfite [9], and 12-crown-4 [10] and inorganic components such as CO_2 and N_2O [11] are reported to form 'good' SEI on a graphite electrode.

On the contrary to works of film forming additives, we have shown that exfoliation of graphite can be suppressed by adjusting solvation structure of Li^+ ions in PC-based electrolytes without film

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forming additives. We reported that success of Li^+ ion intercalation in PC-based electrolytes depends on the concentration of lithium salt [12]. The solvation number of Li^+ ions is often reported as ca. 4 [13–15] and intercalation of Li^+ ions takes place when the molar ratio of PC/ Li^+ in the PC-based electrolyte is less than 4 [16]. The low molar ratio of PC/ Li^+ than 4 should cause difference on the solvation structure of Li^+ ions [16]. Furthermore, we reported that Li^+ ion intercalation can be achieved by addition of stronger Lewis acid, Ca^{2+} ion, to PC-based electrolytes containing Li^+ ions [17]. This phenomenon can also be attributed to the change of Li^+ ion solvation structure under the effect of Ca^{2+} ions, attracting PC molecules more strongly than Li^+ ions.

Although Li^+ ion intercalation into a graphite electrode in PC-based electrolytes without film forming additives become possible by increasing salt concentration, another problem of drastic increase in the electrolyte viscosity emerges. Viscosity of 1.1 mol dm^{-3} LiPF_6/PC is 9.93 mPa s [18] in which exfoliation of graphite takes place, and that of 2.91 mol dm^{-3} LiPF_6/PC is 223 mPa s [18] in which Li^+ ion intercalation takes place. Viscosity increases also by adding Ca^{2+} ions to the electrolyte, and it can be a drawback for practical use.

Electrolytes used in LIBs consist of linear esters such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC). This is because those organic solvents have low viscosity [19,20] and can decrease viscosity of EC-based electrolytes to improve battery performance. Decreasing viscosity of the PC-based electrolyte containing calcium salt is required for a practical use. Hence, we chose DMC, which is one of the widely used linear esters, as a co-solvent to decrease viscosity of the electrolyte.

In this paper we report Li^+ ion intercalation in PC-DMC-based electrolyte with Ca^{2+} ions. Our previous work shows effect of Ca^{2+} ion addition to Li^+ ion intercalation in PC-based electrolytes [17]. The effect of DMC addition on Li^+ ion intercalation to PC-based electrolyte containing Ca^{2+} ions is investigated. Intercalation of Li^+ ions is discussed in terms of solvation structure in the electrolytes.

2. Experimental

A three electrode cell was used for all electrochemical measurements. A composite electrode consists of natural graphite (NG-7) and poly(vinylidene difluoride) (PVDF) by the weight ratio of 9:1 was used as a working electrode. Lithium metal was used both for counter and reference electrodes. All potentials are referred to Li/Li^+ .

Electrolytes were prepared from lithium bis(trifluoromethanesulfonyl)amide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiTFSA), calcium bis(trifluoromethanesulfonyl)amide ($\text{CaN}(\text{SO}_2\text{CF}_3)_2$, Ca(TFSA)₂), PC and DMC. Electrolytes based on the molar ratio of PC:LiTFSA:Ca(TFSA)₂=12:1:0.5 and 1 mol dm^{-3} LiTFSA + 0.5 mol dm^{-3} Ca(TFSA)₂/PC + DMC (LiTFSA:Ca(TFSA)₂:PC:DMC = 1:0.5:1.1:10 in molar ratio) were prepared. The molar ratio of PC:LiTFSA = 12:1 is equivalent to 1 mol dm^{-3} LiTFSA/PC. The amount of DMC was varied from DMC/PC = 4 to 10 in molar ratio (DMC/LiTFSA = 48–120 in molar ratio) for the electrolyte based on PC:LiTFSA:Ca(TFSA)₂=12:1:0.5. All reagents were used as received from Kishida Chemical Co., Ltd. All the reagents were dehydrated enough to study electrochemical reactions. Charge–discharge rate was $1/30 \text{ C}$ for electrolytes prepared with PC:LiTFSA:Ca(TFSA)₂ = 12:1:0.5 and DMC and $1/13 \text{ C}$ for 1 mol dm^{-3} LiTFSA + 0.5 mol dm^{-3} Ca(TFSA)₂/PC + DMC (PC:DMC = 1:10). 1 C is a current density to intercalate Li^+ to form LiC_6 in 1 h. The measurement was carried out between 0.0 and 3.0 V.

X-ray diffraction measurement was carried out in Ar atmosphere to confirm LiC_6 formation. Rigaku X-ray diffractometer with $\text{CuK}\alpha$ radiation was used. The scanning speed was 2° min^{-1} and the working condition was $40 \text{ kV}/40 \text{ mA}$.

Solution resistance was measured with impedance spectroscopy using 2032 coin-type cell. Anton Paar AMVn was used for measuring viscosity of electrolytes. The measuring temperature was set at 30°C which is the same with the glove box.

3. Results and discussion

In our previous study, we reported that Li^+ ion intercalation took place in an electrolyte with a molar ratio of PC:Li⁺:Ca²⁺ = 12:1.0:1.1 [17]. Conductivity and viscosity of the electrolyte was $0.4 \times 10^{-2} \text{ S cm}^{-1}$ and 58 mPa s , respectively. In order to decrease viscosity of the electrolyte, the amount of calcium salt is decreased and DMC is added in this paper. Intercalation of Li^+ takes place as the amount of Ca^{2+} increases [17]. Effect of the amount of DMC on Li^+ intercalation is studied in the following paragraph.

The molar ratio of PC, LiTFSA and Ca(TFSA)₂ was fixed at PC:LiTFSA:Ca(TFSA)₂ = 12:1:0.5, and DMC was added to the electrolyte. Fig. 1 shows potential curves of a graphite electrode in the electrolytes of DMC/PC = 10 and 6 (DMC/LiTFSA = 120 and 72, respectively) by molar ratio. A charge curve in the electrolyte where the molar ratio of DMC/PC is 6, is shown with a dashed line. The potential did not fall below 0.7 V and a potential plateau appeared at 0.8 V. The similar behavior was observed in our previous result in the electrolyte where the molar ratio of components were PC:LiTFSA:Ca(TFSA)₂ = 12:1.0:1.0 [17]. A plateau was observed at 0.8 V and exfoliation of graphite took place in this electrolyte [17]. We did not observe any intercalation behavior when DMC/PC = 6, and it suggests that constant decomposition of electrolyte and/or exfoliation of graphite took place. In contrast, plateaus were observed below 0.3 V in the electrolyte of DMC/PC = 10. Since Li^+ ions are the only intercalate in PC-based electrolytes containing both lithium and calcium salt [17], and the potential is equivalent to electrochemical Li^+ ion intercalation [21], this reversible reaction can be attributed to Li^+ ion intercalation/de-intercalation. Fig. 1 shows a clear shift of an electrochemical behavior of a graphite electrode by DMC addition to the electrolyte.

Success/failure of Li^+ ion intercalation in the electrolytes with varied molar ratio of DMC/PC from 4 to 10 is summarized in Table 1. O means intercalation of Li^+ ion took place, X means that exfoliation of graphite took place, and O/X means the result was in

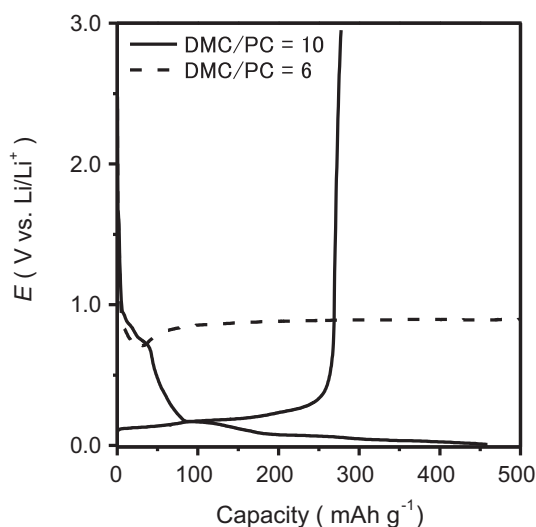


Fig. 1. Potential curves of natural graphite (NG-7) in electrolytes of DMC/PC = 10 (solid line) and 6 (dashed line).

Table 1

Molar ratios of electrolyte component and results of electrochemical intercalation behavior. O represents Li^+ intercalation, X represents exfoliation of graphite, O/X represents intermediate of O and X.

Molar ratios					Li^+ intercalation
PC	LiTfSA	$\text{Ca}(\text{TfSA})_2$	DMC/PC	DMC	
12	1.0	0.5	4.0	48	X
12	1.0	0.5	5.0	60	X
12	1.0	0.5	6.0	72	X
12	1.0	0.5	7.0	84	X/O
12	1.0	0.5	8.0	96	X/O
12	1.0	0.5	9.0	108	O
12	1.0	0.5	10	120	O

between circle and cross; some trials exhibited exfoliation of graphite and others exhibited Li^+ ion intercalation. Intercalation of Li^+ ions became possible as the amount of DMC in the electrolyte increases. Since the molar ratio of PC, LiTfSA, and $\text{Ca}(\text{TfSA})_2$ was fixed, intercalation of Li^+ ions is attributed to the increased amount of DMC in the electrolyte. It was also confirmed that Li^+ ion intercalation does not take place when DMC was added as $\text{DMC/PC} = 10$ in the molar ratio ($\text{DMC/LiTfSA} = 120$ in molar ratio) to 1 mol dm^{-3} LiTfSA/PC, which does not contain calcium salt. Hence, together with our previous result [17], both molar ratios of $\text{Ca}^{2+}/\text{Li}^+$ and DMC/PC affect intercalation behavior on a graphite electrode.

Fig. 1 shows a discharge capacity lower than 300 mAh g^{-1} , which is much lower than the theoretical capacity of graphite, 372 mAh g^{-1} . Conductivity and viscosity of the electrolyte was $0.5 \times 10^{-2} \text{ S cm}^{-1}$ and 2.6 mPa s , respectively. Viscosity of the electrolyte was less than 1/20 of the electrolyte of PC: $\text{Li}^+:\text{Ca}^{2+} = 12:1.0:1.1$ in molar ratio [17]. However, conductivity was as low as the previous electrolyte because molarity of the electrolyte was decreased by diluting the electrolyte with DMC, and can cause overpotential during intercalation process. Hence, the ratio of DMC/PC was kept at 10 and molarity of salts was increased, and the electrochemical behavior of a graphite electrode was studied more in detail.

Fig. 2 shows charge–discharge curves of NG-7 in 1 mol dm^{-3} LiTfSA + 0.5 mol dm^{-3} $\text{Ca}(\text{TfSA})_2/\text{PC} + \text{DMC}$ (PC:DMC = 1:10 in molar ratio). In the first reduction process, plateaus are observed around 0.7 V and between 0.3 and 0.0 V. The reduction around 0.7 V was only observed in the first reduction process of a graphite

electrode, and irreversible reaction did not take place after 1st cycle. The reversibility of the first cycle was 75%. The irreversible reduction in the first cycle may be related to formation of a surface film on graphite. Plateaus between 0.3 and 0.0 V are observed in both reduction and oxidation process. In order to confirm that the intercalation process was carried out only by Li^+ ions, the graphite electrode was kept at 0 V to obtain homogeneous graphite intercalation compound (GIC). Interlayer distance of the resultant GIC was investigated with XRD.

X-ray diffraction pattern of the electrode kept at 0 V in 1 mol dm^{-3} LiTfSA + 0.5 mol dm^{-3} $\text{Ca}(\text{TfSA})_2/\text{PC} + \text{DMC}$ (DMC/PC = 10) is shown in Fig. 3. Peaks of Cu substrate are denoted as Cu. The numbers on peaks denote 00l index. Peaks are observed at 24.1° and 49.2° in 2θ , and d values are calculated to be 0.369 and 0.185 nm, respectively. The interlayer distance of graphite layers with Li^+ ions in between is reported to be 0.370 nm [22]. Observed d values are in good agreement with the reported interlayer distance of Li-GIC and these peaks are attributed to stage 1 Li-GIC 001 and 002 as shown in Fig. 3. The interlayer distance of graphite layers is 0.452 nm when the intercalates are Ca^{2+} ions [23], and the observed d values do not accord with the reported distance. Thus it was confirmed that Li^+ ions were the only intercalate in this PC/DMC-based electrolyte and Ca^{2+} ions did not intercalate into graphite layers. From Fig. 3, it was also confirmed that plateaus observed below 0.3 V are attributed to intercalation/de-intercalation of Li^+ ions.

According to Raman spectroscopy, the average solvation number of PC on Li^+ ions in 1 mol dm^{-3} LiTfSA/PC + DMC (DMC/PC = 9) is 0.9 [24]. The average solvation number of Li^+ ions in this electrolyte is considered to be smaller than 0.9 because the molar ratio of DMC/PC is larger in the electrolyte. Existence of Ca^{2+} ions in the electrolyte should also affect the solvation structure of Li^+ ions. The solvation enthalpy of PC to Li^+ ion is higher than that of DMC to Li^+ ion [24,25]. Thus solvation enthalpy of PC to Ca^{2+} ion is higher than that of DMC, and Ca^{2+} ion prefers to be solvated with PC more than DMC. Interaction between PC and Ca^{2+} ion is higher than that of Li^+ ion because Ca^{2+} ion is a bivalent ion, and PC molecules are considered to solvate Ca^{2+} ions more than Li^+ ions. Hence, the average solvation number of PC on Li^+ ion in this electrolyte is considered to be smaller than that without calcium salt. The important point is that exfoliation, which takes place when Li^+ ions are solvated by 4 PC molecules, no longer takes place by DMC and

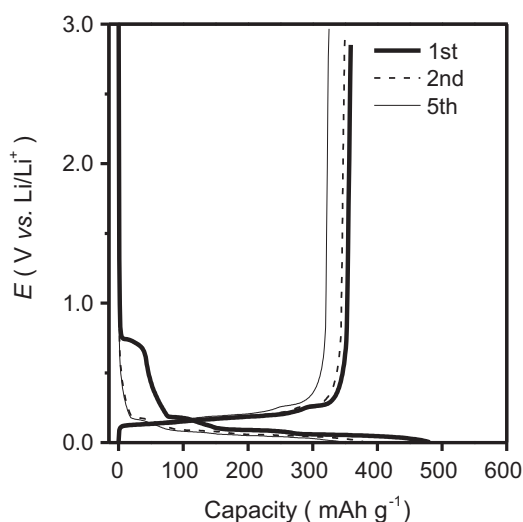


Fig. 2. Charge and discharge curves of natural graphite (NG-7) in 1 mol dm^{-3} LiTfSA + 0.5 mol dm^{-3} $\text{Ca}(\text{TfSA})_2/\text{PC} + \text{DMC}$ (DMC/PC = 10).

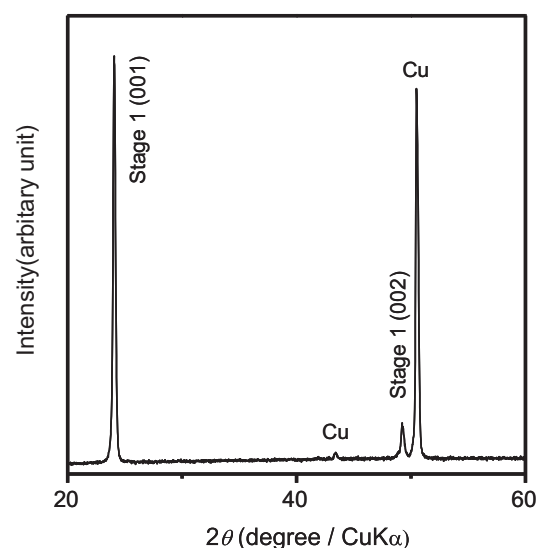


Fig. 3. X-ray diffraction pattern of NG-7 after kept at 0 V in 1 mol dm^{-3} LiTfSA + 0.5 mol dm^{-3} $\text{Ca}(\text{TfSA})_2/\text{PC} + \text{DMC}$ (DMC/PC = 10).

Table 2

Molar ratios of components, conductivity, and viscosity of the electrolytes in which Li^+ intercalation took place.

Molar ratios					Conductivity [S cm^{-1}]	Viscosity [mPa s]
PC	LiTfSA	$\text{Ca}(\text{TfSA})_2$	DMC/PC	DMC		
1.1	1.0	0.5	10	11	1.1×10^{-2}	3.9
12	1.0	1.1	0.0	0.0	0.4×10^{-2}	58
12	1.0	0.5	10	120	0.5×10^{-2}	2.6

calcium salt addition. Intercalation of Li^+ ion into graphite can take place in 1 mol dm^{-3} LiAsF_6 /DMC containing a trace of impurities, which is also necessary for 1 mol dm^{-3} LiAsF_6 /EC $^{-1}$ [26]. Although exact solvation number is unknown, successful Li^+ ion intercalation can be attributed to smaller solvation number of PC on Li^+ ions. It is possible that Li^+ ions intercalate into graphite when Li^+ ions are solvated only by DMC, and one of the possible explanations for the Li^+ ion intercalation is difference of reduction product caused by smaller amount of PC around Li^+ ions.

Conductivity and viscosity of 1 mol dm^{-3} $\text{LiTfSA} + 0.5 \text{ mol dm}^{-3}$ $\text{Ca}(\text{TfSA})_2$ /PC+DMC (DMC/PC=10) (PC:LiTfSA:Ca(TfSA) $_2$ = 1.1:1.0:0.5, DMC/PC = 10 in molar ratio) were $1.1 \times 10^{-2} \text{ S cm}^{-1}$ and 3.9 mPa s , respectively. Viscosity and conductivity of electrolytes studied in our previous result [17] (PC:LiTfSA:Ca(TfSA) $_2$ = 12:1.0:0.5) and Fig. 1 (PC:LiTfSA:Ca(TfSA) $_2$ = 12:1.0:0.5, DMC/PC = 10) are summarized in Table 2. The electrolyte of 1 mol dm^{-3} $\text{LiTfSA} + 0.5 \text{ mol dm}^{-3}$ $\text{Ca}(\text{TfSA})_2$ /PC + DMC shows the highest conductivity and lowest viscosity among electrolytes shown in Table 2. Charge rate in Fig. 1 is 1/30 C and it was 1/13 in Fig. 2, but Fig. 2 shows better discharge capacity. The lower capacity of Fig. 1 may due to lower conductivity causing more overpotential than in Fig. 2. The electrolyte of Fig. 2 shows more than 10 times less viscosity and more than doubled conductivity of the electrolyte from our previous study. Both viscosity and conductivity of the electrolyte affects performance of a graphite electrode, and it was certainly improved by DMC addition.

4. Conclusions

Electrochemical behavior of a graphite electrode in PC-DMC-based electrolytes containing both Li^+ and Ca^{2+} ions was studied. Intercalation of Li^+ ions took place when a certain amount of DMC was added in PC-based electrolyte containing calcium salt. It was found out that both DMC and calcium salt are important for Li^+ ion intercalation. Performance of a graphite electrode was improved by increasing conductivity of the electrolyte, and the electrolyte is considered to show better performance at low temperature than

the electrolyte of PC:LiTfSA:Ca(TfSA) $_2$ = 12:1:1.1 we previously reported [17].

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